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(54) Curable polyorganosiloxane compositions

(57) A composition comprising (A) a polyorganosiloxane having per molecule at least one substituent of the general formula -YZ, linked to a silicon atom through a Si-C bond wherein Y denotes a divalent organic radical and Z denotes a radical containing a divalent olefinically polyunsaturated group wherein two olefinically unsaturated bonds are separated by not more than 3 carbon atoms, and (B) a photoinitiator, is useful for coating substrates and is curable by UV irradiation. The composition preferably also contains a mercapto-functional polysiloxane.

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SPECIFICATION

Curable polyorganosiloxane compositions

5 The present invention relates to curable compositions containing polyorganosiloxanes with substituents having olefinic polyunsaturation and to the use of such compositions for coating substrates. 5

Polyorganosiloxanes which are curable to a crosslinked material and which contain olefinically polyunsaturated substituents are known.

European patent application E.P. 152 830 describes polyorganosiloxanes containing, per molecule, at least 10 one monovalent olefinically polyunsaturated organic radical containing at least one 1,3-pentadienylene group or 1,4-pentadienylene group bonded to silicon through silicon-to-carbon bond. These polyorganosiloxanes are said to be curable to a crosslinked material at ambient temperature upon exposure to gaseous oxygen. The curing of these polyorganosiloxanes is shown in the examples to be effected in a time which varies according to the formulation from about 2 hours to more than 72 hours. In some cases these 15 materials had not yet cured fully within said 72 hours. Thickened, but still liquid, material was obtained.

It is desirable to cause such polyorganosiloxanes to cure more rapidly, especially where coating processes for certain substrates are involved as for example in the coating of paper.

We have now found that if polyorganosiloxanes having substituents containing a divalent olefinically polyunsaturated moiety are exposed to ultra-violet radiation in the presence of a photoinitiator, a much 20 faster cure rate can be obtained.

The invention accordingly provides in one of its aspects a composition comprising (A) a polyorganosiloxane having per molecule at least one substituent of the general formula -YZ, linked to a silicon atom through a Si-C bond, wherein Y denotes a divalent organic radical consisting of C, H and O atoms and optionally includes N atoms and Z denotes a monovalent hydrocarbon radical containing a divalent olefinically 25 polyunsaturated group wherein two olefinically unsaturated bonds are separated by not more than 3 carbon atoms, and (B) a photoinitiator. In another aspect the invention provides a process for coating a surface which comprises applying thereto said composition and exposing the treated surface to ultra-violet radiation.

Polyorganosiloxanes (A), for use in a composition according to the invention, are known in the art and may 30 be described as having units of the general formula (I)



wherein R denotes a monovalent hydrocarbon radical having from 1 to 9 carbon atoms, R' denotes H, OH, or organic radical having from 1 to 30 carbon atoms, H atoms and, optionally, O, F or N atoms and Y and Z are as defined above; a, b and c have independently a value of 0, 1, 2 or 3 provided a + b + c is not larger than 3 and 40 at least one -YZ substituent is present per molecule.

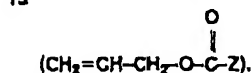
Examples of the group R include alkyl groups e.g. methyl, ethyl, propyl, isobutyl; aryl groups e.g. phenyl; aralkyl groups e.g. phenylethyl and alkaryl groups e.g. methylphenyl. Examples of R' include H, OH, hydroxyfunctional hydrocarbon groups, alkoxy groups, aryloxy groups, alkoxyalkoxy groups, fluorinated alkyl 45 groups, amino-functional or diamino-functional groups, groups containing mono-unsaturated moieties, epoxy-functional groups. Such groups are for example methoxy, ethoxy, butoxy, ethoxyethoxy, trifluoropropyl groups, aminopropyl groups, aminoethyl aminopropyl groups, vinylalkyl groups, glycidoxypropyl groups.

Z is a hydrocarbon radical containing a divalent olefinically polyunsaturated group wherein two unsaturated bonds are separated by no more than 3 carbon atoms. Such groups may have conjugated or unconjugated polyunsaturation. Examples of Z include such radicals as 8, 11 heptadecadienyl, 8, 11, 14 heptadecatrienyl and 8, 10, 12 heptadecatrienyl. To obtain polyorganosiloxanes (A) having the exemplified Z groups, polyorganosiloxanes having functional substituents may be reacted with e.g. linoleic acid, linolenic acid, eleostearic acid, or esters of these acids. However, other compounds having the required divalent 55 olefinically polyunsaturation may also be reacted with polyorganosiloxanes having functional substituents. Examples of such other compounds include 2,4 hexadienoic acid and cyclohexadienoic acid.

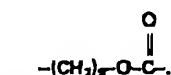
Y is determined by the way polyorganosiloxanes (A) is made. Different modes of producing these polyorganosiloxanes are possible. One such method involves the reaction of a polyorganosiloxane having an organic substituent with a functional group, e.g. a hydroxy, amino or diamino group or a Si bonded hydrogen atom with a compound of the general formula Z-Q, wherein Z is as defined above and Q is a reactive group which is capable of reacting with the functional group of the polyorganosiloxane. Examples of Q are -COOH and -COOR. If for example a polyorganosiloxane having an aminopropyl group linked to Si is reacted with Z-COOH, Y would be



According to another method of preparing the polyorganosiloxanes (A) a siloxane with silicon-bonded hydrogen is reacted with a compound



In the resulting product Y would be the group



Yet another method for making polyorganosiloxanes (A) includes the reaction of previously prepared silanes e.g. of the general formula Z-Y-Si(R)₂ under hydrolysis conditions with e.g. dimethyldichlorosilanes or trimethylchlorosilanes and condensation of the hydrolysis products to the desired polyorganosiloxanes (A). In the preferred polyorganosiloxanes (A), Y is the group



Polyorganosiloxanes (A) may vary from low viscosity fluids to high viscosity materials or resinous partially crosslinked materials. The number of units (I) may vary from 2 to 1000 or more. Values for a, b and c and for a + b + c may vary from 0 to 3 as long as the resulting polyorganosiloxanes (A) are sufficiently workable to be used in a coating process. Preferred polyorganosiloxanes (A) have an average chain length of 20 - 600 Si atoms and are substantially linear polydiorganosiloxanes where at least 80% of the silicon bonded substituents are methyl groups, from 0.01 to 20% are -YZ groups and any remaining substituents are chosen from ethyl and phenyl groups.

Preferred polyorganosiloxanes (A) may also comprise a number of R' substituents, which are unreacted functional groups, which were present on the polysiloxane precursor of (A) before reaction with for example the compound Z-Q as is defined above. Such groups R' will e.g. be present if less than stoichiometric amounts of said compound have been reacted with the polysiloxane precursor of (A).

In most preferred polyorganosiloxanes (A) from about 1 to 10% of the silicon-bonded substituents are Y-Z groups and substantially all other silicon-bonded substituents are methyl groups.

Component (B) of the compositions of this invention comprises one or more photoinitiator substances. A number of substances which function as photoinitiators are known in the art and include e.g. aromatic ketones e.g. acetophenone, benzophenone and 4,4'-diaminobenzophenone, benzoin compounds e.g. benzoin, benzoin methyl ether and benzoin ethyl ether, quinone and anthrone compounds e.g. hydroquinone, anthraquinone, naphthoquinone and 3-methyl-1,3-diazo-1,9-benzanthrone, phenolic compounds e.g. 2,4-dinitrophenol and azo compounds e.g. azo-bis-isobutyronitrile. The preferred photoinitiators for use in the compositions of this invention are those which are freely miscible with the component (A) of the composition. The use of compatible photoinitiators avoids the difficulties which may arise due to separation of this component on storage.

Compositions according to the invention may be prepared by simply mixing component (A) and component (B). The compositions according to the invention will, however, react in the presence of ultra-violet radiation and are therefore preferably stored in light-proof containers or storage areas. The photoinitiator (B) may be employed in conventional amounts, from about 0.1 to about 5 percent by weight, based on the weight of polyorganosiloxane (A).

In a preferred embodiment of this invention the composition comprising components (A) and (B) also comprises another component (C) which is an organosiloxane having in the molecule at least 2 siloxane units of the general formula (II)



10 wherein X represents a divalent saturated aliphatic hydrocarbon group having from 3 to 8 inclusive carbon atoms, X' represents a monovalent hydrocarbon group having from 1 to 6 inclusive carbon atoms and free of aliphatic unsaturation, an alkoxy group having from 1 to 4 carbon atoms or an alkoxyalkoxy group having from 2 to 6 carbon atoms and a has a value of 0, 1 or 2, any remaining units having the general formula



wherein X'' represents a monovalent hydrocarbon group having from 1 to 8 carbon atoms and free of aliphatic unsaturation and b has a value of 0, 1, 2 or 3 at least 50 percent of the total X' and X'' groups being methyl.

20 The organosiloxanes employed as component (C) of a composition according to this invention have in the molecule at least two mercaptoalkyl siloxane units falling within the general formula (II). In the general formula X may be any divalent saturated aliphatic group having from 3 to 8 carbon atoms, for example $-(\text{CH}_2)_3-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, $-(\text{CH}_2)_4-$ and $-(\text{CH}_2)_6-$. The substituent X', when present, may be for example methyl, ethyl, propyl, phenyl, methoxy, ethoxy or methoxyethoxy. The organosiloxanes (C) may be homo-
25 polymers consisting only of units (II), for example as in the cyclic siloxanes, or they may be copolymers containing both units (II) and units falling within the general formula (III). In the copolymeric units (III), X'' may be any monovalent hydrocarbon group having from 1 to 8 carbon atoms and free of aliphatic unsaturation, for example methyl, ethyl, propyl or phenyl. At least 50 percent, and preferably substantially all, of the total X' and X'' substituents should be methyl. It is therefore preferred that each X' and each X'' is methyl.

30 The mercaptoalkyl substituents in organosiloxanes (C) may be attached to any of the silicon atoms in the molecule, that is they may be present in chain terminating units $\text{HSX(X')}_2\text{SiO}_{0.5}$, in HSX(X')SiO or in $\text{HSXSIO}_{1.5}$ units. The organosiloxanes (C) may vary in molecular size from the dialloxanes to high molecular weight polymers and may range in consistency from freely-flowing liquids to resinous solids. When the compositions of this invention are intended for the provision of coatings on paper and other flexible substrates the preferred organosiloxanes (C) are polydiorganosiloxanes having from about 50 to about 500
35 siloxane units and a viscosity of from about 50 to about 10,000 cSt at 25°C, (i.e. $5 \times 10^{-5} \text{ m}^2/\text{s}$ to $10^{-2} \text{ m}^2/\text{s}$) at least three of the acid siloxane units, and preferably from 5 to 20 percent of the total siloxane units of organosiloxane (C) more preferably from 5 to 10 percent thereof having therein a HSX- group attached to silicon.

40 Organosiloxanes (C) are in general known substances and methods for preparing such organosiloxanes will be evident to those skilled in the art. For example, according to one method a silane bearing silicon-bonded hydrolysable atoms or groups and a mercaptoalkyl group HSX- is hydrolysed and condensed to prepare a mixture of cyclic and linear siloxanes which is then mixed with cyclic and/or linear siloxanes having units



and the mixture equilibrated employing a suitable catalyst. The mixture preferably contains a source of endblocking units e.g. hexamethyldisiloxane but such source may be omitted e.g. where a high molecular
50 weight organopolysiloxane is required. Another, less preferred method comprises reacting a hydroxyl-terminated polydiorganosiloxane with a silane $\text{HSXSIR}_a(\text{OR})_{3-a}$ wherein OR is an alkoxy group and a is 0 or 1.

Compositions comprising components (A), (B) and (C) exhibit a faster cure than those compositions which do not include component (C). The compositions of this preferred embodiment of the invention may be
55 prepared by simply mixing components (A), (B) and (C) in any order. In the undiluted state components (A) and (C) react together in the presence of (B) and ultra-violet radiation. They may, however, be stored in the mixed state in the absence of such radiation, for example in lightproof containers or storage areas. For maximum storage stability it is preferred to provide the compositions as a two package system, the organosiloxanes (A) and (C) being packaged separately and the photoinitiator (B) being present with component (C). The amounts of component (C) which may be used may vary from traces up to such quantities which
60 will give at least a ratio of one $-\text{SiXSH}$ group in (C) per unsaturated bond in (A). An excess of the former will also work, but is unlikely to give an improved cure rate. Preferably, however, the ratio of SH groups in (C) present in the composition over the number of unsaturated bonds present in Z of (A) is from about 1/5 to 1/1.

The cure rates of the compositions of this invention when exposed to ultra-violet radiation are found to be superior to the cure rate of polyorganosiloxanes (A) when exposed to oxygen. Even when the compositions of this invention are exposed to ultra-violet radiation in the absence of oxygen, for example under a nitrogen blanket, cure rates still exceed those of polyorganosiloxanes (A) under oxygen. Compositions comprising

5 components (A), (B) and (C) are seen to cure within minutes when exposed to ultra-violet radiation.

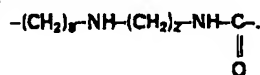
Curing of compositions comprising polydiorganosiloxanes bearing mercaptoalkyl radicals and polyorganosiloxanes having substituents with unsaturation by exposure to ultra-violet radiation, is known in the art and is described for example in U.S. patent 4 052 529. However, an advantage of compositions according to the present invention is that they may be cured by exposure to ultra-violet radiation or by exposure to

10 oxygen or a combination of both. This property makes it possible, for example in the case of coating three dimensional objects where certain areas are inaccessible or less accessible to the ultra-violet light rays, to continue curing the coating after the exposure to ultra-violet radiation has ceased as long as the object is kept in contact with oxygen; for example by exposure to the normal atmosphere. Advantage may also be taken of

15 on exposure to oxygen. In order to accelerate the secondary cure by exposure to oxygen, metal compounds which are known in the paint and varnish industry as driers, may be incorporated into the compositions of this invention according to known techniques in such industries. Examples of such driers are carboxylic acid salts of cobalt, copper, tin, zinc etc. Such driers do not adversely affect the cure of the composition when exposed to UV light.

20 However, driers which are reactive with mercaptoalkyl groups are preferably omitted from compositions of this invention in which organosiloxane (C) is present. In the event of reaction taking place the effectiveness of (C) in acceleration the cure rate can be significantly diminished.

25 Such drying agents are also not recommended for use with those compositions comprising polyorganosiloxane (A) in which Y is a group of the formula



30 The drying agents are believed to form a complex with these polyorganosiloxanes (A) and inhibit their cure when exposed to oxygen.

The compositions of this invention are comparatively easy to prepare and may be applied to a variety of substrates. They may be cured thereon by exposure to ultra-violet radiation to produce adherent coatings. Although curing will take place slowly in the presence of normal daylight it is preferred to accelerate the cure rate by exposure to lamps which emit U.V. light, preferably with a wavelength in the range from 250 to 450

35 nm for example medium pressure mercury lamps. The compositions may be applied to substrates such as metals e.g. aluminium, iron, steel and copper, plastics e.g. nylon, polyester, polyethylene and polypropylene, siliceous materials e.g. cement, textiles e.g. cotton and synthetics and cellulosic materials such as paper, plastics coated paper and paper board. They are particularly useful for the formation of release coatings or for conformal coatings e.g. on electrical and electronic circuits. The compositions may be applied to the substrate employing any suitable means such as dip coating, spraying, doctor blade or gravure roll.

40 In addition to components (A) and (B) or to components (A), (B) and (C) of the preferred embodiment of the compositions of this invention the compositions may also contain ingredients normally present in curable coating compositions. For example, the compositions may contain dyes or colorants and may be diluted with

45 organic solvents to facilitate application to some substrates. However, when a significant amount of solvent is present it may be necessary to subject the coated substrate to elevated temperatures prior to curing in order to effect solvent removal therefrom. Other ingredients which may be present include fillers, pigments and additives for modifying the release properties of the coating.

The following examples wherein Me denotes a methyl radical and parts and percentages are expressed by

50 weight, unless otherwise specified, illustrate the invention.

Example 1

8.94g (64.9 mmol) hexamethyldisiloxane, 1154g (15 mol) $(\text{Me}_2\text{SiO})_n$, 37.8g (322 mmol) $(\text{H}_2\text{N}(\text{CH}_2)_2\text{SiO})_n$ and 12.0g K-silanolate (contains 20 mmol K) were placed in a 2 ltr flask with stirrer and thermometer and heated

55 under nitrogen atmosphere to 130°C for 2 hours and thereafter to 170°C for 4 hours. The viscous mixture was cooled to 100°C, 94g (338 mmol) linseed oil acid was added and the mixture reheated to 140°C. A distillation bridge was connected to the flask and under slowly reducing pressure first the reaction water and then low boiling siloxanes were distilled off (150°C/3mm Hg). After 3 1/2 hours a total of 138g distillate had been

60 collected. The cloudy viscous product was diluted with ether and filtered through diatomaceous earth. The solvent was removed from the filtrate by distillation under reduced pressure (150°C/3mm Hg) and finally 1081g of a pale yellow viscous liquid remained in the flask. This liquid was a trimethylsiloxy terminated copolymer of Me_2SiO units and $\text{Me}(\text{AC}(\text{O})\text{NHC}_2\text{H}_5)\text{SiO}$ units, where A has the average formula $\text{C}_{16.5}\text{H}_{30.2}$.

Example 2

3 samples were prepared from the copolymer product from Example 1 as follows. A first comparative sample (Sample A) was poured onto a glass plate to form a film of about 0.6mm thickness. A second sample according to the invention (Sample B), was prepared by heating 89 parts of the product of experiment 12 and 1 part benzophenone to 50°C and stirring vigorously to obtain a homogeneous solution, a part of which was poured onto a glass plate to a thickness of about 0.5mm. A third sample according to the preferred embodiment of the invention (Sample C), was prepared by heating 88 parts of the product of Example 1, 33 parts mercapto functional polysiloxane (DP 125, 8 mol % S-H) and 1 part benzophenone to 50°C and stirring vigorously to provide a homogeneous viscous liquid, from which a part was poured onto a glass plate to a thickness of ca. 0.5mm. These films were exposed to sunlight. Within two weeks Sample (A) was cured to a soft, tack free rubber with good adhesion to the glass plate. Within a few hours Sample (B) was cured to a tack free rubber with good adhesion to the glass plate. Within 15 to 30 minutes the surface of Sample (C), and after 1 hour the total sample was cured to a tack free rubber with good adhesion to the glass plate.

Example 3

Samples (A), (B) and (C) as prepared in Example 2 were coated onto Super Calender Kraft paper using a blade coater at a level of about 0.8g per square metre. The coated paper was exposed to light from a medium pressure mercury vapour lamp rated at 80 w/cm, held at a distance of 50mm and focused by an elliptical reflector. The coating was exposed for 0.4 seconds. All samples showed varying degrees of smearing after exposure. Sample (A) showed the most and Sample (C) showed the least smearing. After storing the exposed samples under ambient conditions for 1 to 2 hours the smearing was reduced and in the case of Sample (C) almost disappeared. After a few days at room temperature the smearing of Samples (B) and (C) had disappeared, while Sample (A) showed some smearing.

Example 4

2g of Sample (B) as prepared in Example 2 were poured into a shallow aluminium dish and kept under an inert atmosphere during the experiment by covering the dish with a plate of quartz and purging the dish with a constant flow of nitrogen. The sample was then irradiated with UV light (75 watt; distance = 15cm) for 10 minutes. A thin non-tacky film had been formed on the surface of the sample.

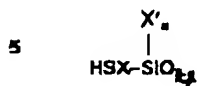
Example 5

88 parts of the product from Example 1, 1 part of benzophenone and 1 part of copper silicate (copper salt of mainly octanoic acid containing 8 weight % Cu) were heated to 50°C and stirred until a homogeneous solution was obtained. A glass test tube was filled with this composition and placed in a flask. This flask was purged with a constant flow of nitrogen and which was covered with a quartz plate. The sample was then exposed to UV light (75 watt, distance = 15cm) for 15 minutes. A thin, almost colourless, non-tacky film was formed on the surface of the sample during the irradiation. The sample was then stored in a glass flask under nitrogen atmosphere to prevent any contact with air but to allow observation of the sample during storage. After one week there was no indication that the sample had undergone any further cure since the irradiation. When an identical sample was stored in a dark place, but in contact with air, after having been exposed to UV irradiation further curing of the sample was observed.

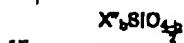
CLAIMS

1. A composition comprising (A) a polyorganosiloxane having per molecule at least one substituent of the general formula $-YZ$, linked to a silicon atom through a Si-C bond, wherein Y denotes a divalent organic radical consisting of C, H and O atoms and optionally includes N atoms and Z denotes a monovalent hydrocarbon radical containing a divalent olefinically polyunsaturated group wherein two olefinically unsaturated bonds are separated by not more than 3 carbon atoms, and (B) a photoinitiator.
2. A composition as claimed in Claim 1 wherein polyorganosiloxane (A) is a substantially linear polydiorganosiloxane having from 20 to about 800 silicon atoms and wherein at least 50% of the silicon-bonded substituents are methyl groups.
3. A composition as claimed in either one of Claims 1 and 2 wherein from 0.01 to 20% of all silicon-bonded substituents in polyorganosiloxane (A) are $-YZ$ substituents.
4. A composition as claimed in Claim 3 wherein 1 to 10% of all silicon-bonded substituents of polyorganosiloxane (A) are $-YZ$ substituents.
5. A composition as claimed in any one of the preceding claims wherein photoinitiator (B) is compatible with polyorganosiloxane (A).

6. A composition according to any one of the preceding claims which also comprises (C) an organosiloxane having in the molecule at least 2 siloxane units of the general formula (II)



wherein X represents a divalent saturated aliphatic hydrocarbon having from 3 to 8 inclusive carbon atoms,
 10 X' represents a monovalent hydrocarbon group having from 1 to 8 inclusive carbon atoms free of aliphatic unsaturation, an alkoxy group having from 1 to 4 carbon atoms or an alkoxyalkoxy group having from 2 to 6 carbon atoms and *a* has a value of 0, 1 or 2, any remaining units when present having the general formula (III)



15 wherein X'' represents a monovalent hydrocarbon group having from 1 to 6 carbon atoms and free of aliphatic unsaturation and *b* has a value of 0, 1, 2 or 3 at least 50% of the total amount of X' and X'' units being methyl.

20 7. A composition as claimed in Claim 6 wherein organosiloxane (C) is a polydiorganosiloxane which has from 50 to about 500 siloxane units and has from 5 to 20% of the total number of siloxane units having therein a HSX- group attached to silicon.

8. A composition as claimed in either of Claims 6 and 7 wherein the ratio of the number of -SH groups in organosiloxane (C) over the number of unsaturated bonds present in Z of polyorganosiloxane (A) is from
 25 about 1/5 to 1/1.

9. A composition substantially as hereinbefore described with reference to any one of Examples 2, 3, 4 and 5.

10. A process for coating a surface which comprises applying thereto a composition as claimed in any one of Claims 1 to 9 and exposing the treated surface to ultra-violet radiation.